



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Immersion Plating with Noble Metals

5 We, ENGELHARD INDUSTRIES, INC., a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 113, Astor Street, Newark 2, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention deals with an immersion plating solution and more particularly with a solution for immersion plating with noble metals.

15 In immersion plating, the metal being plated is provided with a coating or film by chemical replacement, whereby surface metal of the metal being plated is replaced by the plating solution metal, with the said surface metal going into solution.

20 Immersion plating of metals heretofore practiced has been somewhat limited because of the absence of a desirable plating solution or bath. Plating solutions of known composition suffer from rapid undesirable contamination by the replaced metal, resulting in poor adherence or non-uniform deposits on the metal being plated. For example, immersion plating of gold on nickel with the use of conventional immersion plating solutions results in poor adherence of the gold and with the gold film having a brownish appearance instead of the desirable bright yellow gold appearance.

35 Immersion plated films or layers are of greater density than electroplated films or layers and as such have greater corrosion and wear resistance than electroplated films of equal thickness.

40 With the use of immersion plating solutions herein contemplated, the plated articles are provided with uniform thickness deposits regardless of surface concavity and indentation or uneven article contour and configuration as opposed to non-uniform electroplated

deposits, since the electroplated deposits are heavier on the higher electric density areas of the cathode.

50 It is an object of this invention to provide a noble metal plating solution capable of depositing bright noble metal films on base metal. The noble metals which may be used in accordance with this invention are gold, silver, platinum, palladium, iridium, rhodium, ruthenium and osmium, particularly gold, silver, platinum, palladium, rhodium, iridium and ruthenium. It is another object of this invention to provide an immersion plating solution which operates at peak efficiency regardless of the build-up of concentrations of displaced metals going into solution during the plating process. Other objects and advantages of the invention will become apparent from the following description.

65 The invention relates to an immersion plating solution comprising essentially an aqueous solution of a soluble salt of a noble metal, an ammonium buffering and complexing agent, and a chelating agent.

70 Examples of compounds which exert a buffering and complexing action in the plating solution are ammonium hydroxide and the ammonium salts of citric, boric and tartaric acids.

75 More specifically, in the case of a gold solution, the constituents are a gold salt such as sodium or potassium gold cyanide and ammonium hydroxide buffered to a suitable pH with citric, boric, or tartaric acids. A satisfactory solution is provided by dissolving potassium gold cyanide in ammonium hydroxide and adding citric acid to adjust the pH to 6.0. An excess of the ammonium citrate is beneficial. While this type of complex alone will provide a good gold deposit, the quality of the deposit rapidly deteriorates unless a chelating agent is added to complex the metal replacing the gold of the solution.

85 The baths may include various effective chelating agents in combination with a noble

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metal salt and an ammonium buffering and complexing agent. The following are examples of the constituents of the solution, on a one litre basis.

1.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Urea	25 gms.
	water	1 litre
2.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Ethylenedinitrilo tetraacetic acid	25 gms.
	water	1 litre
3.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Ethylenedinitrilo tetraacetic acid	25 gms.
	tetra sodium salt	
	water	1 litre
4.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Acetamide	25 gms.
	water	1 litre
5.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Cyanoacetamide	25 gms.
	Water	1 litre
6.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Dicyandiamide	25 gms.
	Water	1 litre
7.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Sulphosalicylic acid	25 gms.
	Water	1 litre
8.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Urea	25 gms.
	Ammonium hydroxide	to pH 9—10
	Water	1 litre
9.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Ethylenediamine	25 gms.
	Water	1 litre
10.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Ethyl Acetoacetate	25 gms.
	Water	1 litre
11.	KAu (CN) <sub>2</sub>	5 gms.
	Ammonium citrate	20 gms.
	Urea	25 gms.
	Ethylenedinitrilo tetraacetic acid	15 gms.
	(tetra sodium salt)	
	Water	1 litre
12.	Potassium silver cyanide	5 gms.
	Ethylenedinitrilo tetraacetic acid	20 gms.
	NH <sub>4</sub> OH	to pH 8
	Water	1 litre

13.	Silver Acetate	10 gms.
	Ethylenedinitrilo tetraacetic acid	30 gms.
	NH <sub>4</sub> OH	to pH 8
	Water	1 litre
14.	Palladium diamino nitrite	5 gms.
	Ethylenedinitrilo tetraacetic acid	25 gms.
	(tetra sodium salt)	
	NH <sub>4</sub> OH	to pH 9-10
	Water	1 litre
15.	Platinum diamino nitrite	5 gms.
	Ethylenedinitrilo tetraacetic acid	25 gms.
	NH <sub>4</sub> OH	to pH 9-10
	Water	1 litre

While the proportion of the noble metal salts are indicated by the above examples at a preferred 5 gm. weight per litre, it is intended that the proportion of the noble metal salts may range from 10 milligrams to 30 gms. per litre, and the chelating agents must be present in sufficient amount to chelate all the metal replacing the noble metal in solution. The reaction based on plating gold on nickel indicates that at least 1.25 gms. of ethylenedinitrilo tetraacetic acid (tetra sodium salt) is required per gram of gold deposited.

The rate of deposit of the noble metal on the metal base is a function of time and temperature. For example, with the gold baths, the gold is deposited in an amount of about 1 mg. of gold per square inch in one minute and less at a temperature between 90° C. and 100° C. The same baths at 60° C. require about three minutes for a comparable deposit and at 40° C. the baths require about fifteen minutes for such deposits. Generally, between the temperature range of 20° C. and 100° C. the plating time is between less than 1 minute to about 1 hour.

Advantageously a large excess of chelating agent is used and as such the chelating agent is present in an amount of at least three times that of the noble metal salt.

Generally, the immersion plating can be accomplished at temperatures between 20° C. and 100° C. At the lower temperatures, e.g., 25° C. the adherence of gold to the metal base, e.g., nickel, is still sufficient in practice for some types of articles but not so good as in the present embodiment in which the gold immersion plating is carried out at higher temperatures preferably between 60° C. and 100° C. Silver, on the other hand, works very well at room temperatures, e.g., 25° C. The platinum group metals work well at between 60° C. and 100° C.

The following are examples of plating processes according to the invention:

#### EXAMPLE I.

A plating solution was prepared by dissolving 5 grams of potassium gold cyanide in 30 cc of 28% ammonium hydroxide. Water was added to make a 1 litre volume. To the ammoniacal gold cyanide solution, 25 grams of ethylenedinitrilo tetraacetic acid (tetra sodium salt) was added. Citric acid was then added in sufficient quantity to adjust the pH to 6.5, which resulted in the presence of about 10 grams of ammonium citrate per litre. The solution was heated to 70° C. A 1" x 3.5" x 0.010" strip of nickel-plated brass was degreased with carbon tetrachloride vapour and then electrocleaned cathodically in a boiling solution of trisodium phosphate. The strip was then washed with water and immersed in the plating solution for three minutes. After removal from the plating solution, the gold-deposited strip was dried. The difference in weight before immersion and after immersion indicated a gold deposit of about 0.000005" thickness on the strip."

#### EXAMPLE II.

A plating solution was prepared by dissolving 10 grams of silver acetate in 30 cc of 28% ammonium hydroxide. Water was added to make a 1 litre volume. To the ammoniacal silver acetate solution, 20 grams of ethylenedinitrilo tetraacetic acid was added. The pH of the bath was adjusted by adding more ammonia until a pH of 9 was reached. The solution was heated to 30° C. A strip of copper was degreased, electrocleaned and washed in the manner described in connection with the strip in Example I and immersed in the solution for three minutes, removed and dried.

#### EXAMPLE III.

A plating solution was prepared by dissolving 10 grams of platinum diamino nitrite in 30 cc of 28% ammonium hydroxide. Water was added to make a 1 litre volume. To the ammoniacal platinum diamino nitrite solution,

25 grams of ethylenedinitrilo acid (tetra sodium salt) was added. The pH of the solution was adjusted by adding more ammonia until a pH of 9 was reached. The solution  
 5 was heated to 100° C. A strip of copper similar to that of Example II was degreased, electrocleaned and washed in the same manner described in connection with the strip of Ex-  
 10 ample I and immersed in the solution for fifteen minutes, removed and dried. The difference in weight of the strip before and after immersion indicated a deposit of 0.5 mg platinum per square inch.

The noble metal solutions operate over a  
 15 wide pH range, i.e., between 1 and 14, depending upon the noble metal salt employed. For example, gold on nickel operates extremely well at a pH between 5.5 and 9. Gold on tungsten requires a pH of about 14.  
 20 Silver on copper operates at a pH of about 8. Platinum on copper operates at a pH above 9 when the bath temperature is above 95° C.

The noble metal deposits provide a coating which is integral with the metal base over  
 25 which it is plated. By integral it is meant that the bond or adhesive strength between the coat and base is at least equal to the cohesive strength of the coating.

It has been found that the noble metals may  
 30 be deposited on a wide range of metal bases which include the metals nickel, copper and copper alloys, cadmium, zinc, aluminium and aluminium alloys, silver alloys, steel, die cast metals, solders, pewter.

The articles so plated include among  
 35 others costume jewelry, trophies, automobile trim, lamp components, clock components, photo frames, bottle caps, radio knobs, metallized plastic components and electrical plug connectors. Also, the solution may be  
 40 used for colour coding and for providing an intermediate layer for a subsequently applied second metal coat.

While the immersion plating solution is  
 45 herein specifically described in relation to noble metals, it is, of course, herein intended that alloys of noble metals are deposited

on metal bases in a similar manner.

With the combination of constituents in-  
 50 cluding a noble metal salt, an ammonium buffering and complexing agent and a chelating agent in an aqueous solution as heretofore described, the solution operates at  
 55 peak efficiency regardless of the build-up of concentrations of displaced metal going into solution during the plating process.

#### WHAT WE CLAIM IS:—

1. An immersion plating solution compris-  
 60 ing water, a soluble noble metal salt, an ammonium buffering and complexing agent, and a chelating agent.

2. An immersion plating solution accord-  
 65 ing to Claim 1, in which the chelating agent is present in at least a 3 to 1 ratio by weight to the noble metal salt.

3. An immersion plating solution accord-  
 70 ing to Claim 1 or 2, in which the noble metal salt is a gold or a platinum group metal salt.

4. An immersion plating solution accord-  
 75 ing to Claim 3, in which the noble metal salt is sodium or potassium gold cyanide.

5. An immersion plating solution accord-  
 80 ing to any preceding claim, in which the chelating agent is ethylenedinitrilo tetraacetic acid.

6. An immersion plating solution, substan-  
 85 tially as described with reference to any one of Examples 1 to 15, or Example I, II or III of the foregoing Examples.

7. A process for immersion plating a  
 90 metallic base member, which process comprises cleaning the base member and thereafter immersing it in an immersion plating solution claimed in any preceding claim.

8. A process for immersion plating a  
 95 metallic base member, substantially as hereinbefore described with reference to Example I, II or III.

9. A plated metallic base member when-  
 ever produced by the process claimed in Claim 7 or 8 of the preceding claims.

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